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Evaluating a New CEM III/A Cement for Concretes Exposed to Harsh Acid Rich Environments

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Evaluating a new CEM III/A cement for concretes exposed to harsh acid rich environments

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ABSTRACT: The Irish Annex to the European specification, performance, production and conformity of concrete, IS EN 206, recommends CEM III/B cement for acid rich environments containing between 66 to 80% GGBS. However, BS 8500, the UK annex to EN 206 and the British Research Establishment (BRE) Special Digest 1, recommends CEM III/A cement with a GGBS range of 36-65%. This project investigated the performance of a new CEM III/A cement produced by Ecocem Ireland in concretes exposed to such environments using an extensive suite of laboratory tests.

In Ireland, up to €5.8bn will be invested to provide fresh drinking water and clean wastewater. Concrete deterioration in wastewater treatment systems is mostly caused by sulphates and sulphuric acids found in aggressive chemical additives used. Due to the constant operational nature of these facilities, poor concrete performance leads to shut-downs with serious environmental consequences. The Department of Agriculture requires that all farm based concrete complies with the Nitrates Directive and is certified to IS EN 206. This is only possible by using concrete mixes with adequate durability capable of withstanding the harsh environments found in farms, like silage pits, milking parlour floors, etc.

The results from this study show that the CEM III/A cement used performed as well, or better than, other commonly used cements for these environments. It performed particularly well in mass changes following exposure to sulphuric acid and sulphates with higher compressive strengths too.

KEY WORDS: Sulphate attack, sulphuric acid, concrete, mass loss, expansion, contraction.

1 INTRODUCTION

This project investigated whether CEM III/A cement is suitable to be used where harsh, acid rich, environments can be expected. CEM III/A is a blastfurnace cement containing between 36-65% ground blastfurnace slag (GGBS) and is an equivalent to sulphate resisting cement (S.R.C.). Concrete in wastewater systems are susceptible to different forms of attack including biologically produced sulphuric acid and sulphates. The addition of GGBS increases the resistance of concrete to these forms of attack [1, 2].

In such situations concrete sewer corrosion begins when the pH of the alkaline concrete surface is lowered by dissociation of hydrogen sulphide and by carbonation. There is then a build-up of neutrophilic sulphide oxidizing bacteria and fungi colonise on the concrete surface and contribute to a successive oxidation of reduced sulphur compounds to dissociated sulphuric acid. At this point the pH falls below 2 and the sulphuric acid is produced which in turn produces ettringite and gypsum on the concrete surface. The source of the sulphate is the groundwater which contains dissolved sulphate. These two processes occur at the same time and the concrete then begins to crack due to the expansive pressure caused by the growth of ettringite within the cement paste, [3, 4, 5]. This deterioration of concrete may lead to the loss of ability to transport sewerage, contamination of ground and groundwater, excessive ground settlements and cave-ins [6].

The Irish Annex to the European specification, performance, production and conformity of concrete (IS EN 206) recommends that a CEM III/B cement for acid rich environments (66 to 80% GGBS). However, BS 8500 (the UK annex to EN 206) and the British Research Establishment (BRE) Special Digest 1 recommends CEM III/A cement (36 to 65% GGBS).

The objective of the study is to determine if CEM III/A from Ecocem Ireland, (containing between 36-65% GGBS) can be recommended in Ireland to reduce the effect of sodium sulphate and sulphuric acid attack in concrete. The findings could form the basis of concrete design for water and wastewater treatment facilities and the agricultural market particularly those structures in contact with silage. A substantial suite of experimental work was undertaken which assessed the performance of the new cement in these environments and compared against other blended cements, particularly CEM II/A-L on the market.

2 METHODOLOGY

2.1 *Mix proportions*

Samples were cast for five different cement types. A summary of the mixes is shown in Table 1. The mix proportions are shown in Table 2.

Table 1. Summary of concrete cast

Mix ID	Description
1	CEM II A-L + 36% GGBS
2	CEM II A-L + 65% GGBS
3	CEM II A-L + 50% GGBS
4	CEM III/A (Ecocem blend)
5	Sulphate resisting cement (S.R.C)

Table 2. Mix Proportions

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
CEM II	360	360	360	-	-
CEM III	-	-	-	360	-
S.R.C.	-	-	-	-	360
Fines	685	685	685	685	685
Coarse 10mm	405	405	405	405	405
Coarse 20mm	810	810	810	810	810
	(Above quantities in kg/m^3)				
W/C ratio	0.45	0.45	0.45	0.45	0.45
GGBS (%)	36	65	50	-	-

2.2 *Sample preparation*

The research work included casting 40 concrete prisms (285x75x75mm) for expansion and contraction tests and 70 concrete cubes (150x150x150mm) for change in mass and compression strength tests. The concretes were cast in a large pan mixer and compacted using a vibrating table. All samples were placed in a curing tank at 21°C after 24 hours for 28 days.

2.2.1 Sodium sulphate exposure

Four prisms used for expansion and contraction tests were placed into a polyethylene container, see Figure 1(a) and submerged in a sodium sulphate solution, ensuring the quantity was sufficient to cover the prisms by a minimum of 10mm. The solution contained 50g of sodium sulphate (Na_2SO_4) per litre of distilled water. The solution was replaced with a freshly made solution every two months.

2.2.2 Sulphuric acid exposure

Four prisms were cast for expansion and contraction tests in the sulphuric acid solution. Two prisms were placed in a polyethylene container and submerged in a 1% solution of sulphuric acid, ensuring the quantity was sufficient to cover the prisms by a minimum of 10mm. The two remaining prisms were used as a control for both and placed in water for the duration of the test programme. A sulphuric acid solution of 1% by volume, with a pH level of 1.5, is considered as representative of the acidity levels found in aggressive sewer environments [6, 7], and therefore adopted for the laboratory experiments. A pH level of 1.5 represents the most severe conditions to be expected in service but this level may vary in practice due to a number of environmental factors.

2.3 *Expansion and contraction tests*

Expansion and contraction readings were taken from the all samples. Readings were taken using a reference rod (A). The reference rod was then removed and the prism was then placed in the instrument and a reading recorded (B, see Figure 1(b)). The prism was then placed in the solution for 28 days at which point it was removed and measured (C). Finally the sample was placed into the instrument and a reading (D) was taken. The active deformation of the sample was calculated using the formula: [(D – B) – (C – A)]. Additional (C and D) readings were taken every 28 days for 6 months.

(a) (b)

Figure 1. (a) Comparator reader with prism, (b) prisms submerged in sodium sulphate solution

2.4 *Mass loss – sulphuric acid exposure*

Twelve cubes were cast for each mix. 24 hours after casting, all cubes were placed in a curing tank for 28 days. Six cubes from each mix kept in water to act as the control. Six cubes from each mix were placed in a polyethylene container and filled with a 1%, by volume solution of sulphuric acid to cover the cubes by a minimum of 10mm.

After a further 28 days all cubes were removed from their containers and brushed with a wire brush under running water which resulted in milky white runoff (Figure 2). The samples were washed weighed to determine if any mass loss had occurred. Any loosely adhering corrosion products present on the cubes placed in acid were brushed away prior to recording the mass. Samples were then returned to their containers for a further 28 days. Readings were again taken at 28 day intervals for 6 months.

The acid was monitored throughout the testing in order to maintain a PH value of 1.5 +-0.3. Once the solution deviated from this value the whole solution was replaced. This occurred three times in the 6 month period.

2.5 *Compressive strength*

While mass change is the traditional method for measuring the attack in concrete to acids, compressive strength tests are also a reliable performance measure of the resistance of concrete to acid attack [6]. Strength test were carried out on both the control and exposed cubes at 28 days, see Figure 3 and again upon completion of the testing programme at 196 days.

Figure 2: Cube brushed under running water

Figure 3. Cube in compression testing machine at 28 days

3 RESULTS

3.1 *Expansion and contraction tests*

Figures 4 – 6 show the average change in length of the prism exposed to water, sulphuric acid and sodium sulphates respectively. As may be seen from Figure 4, the CEM III/A cement had the highest changes in length over the exposure time in comparison with the other cement types for exposure to water. Only CEM II A-L + 36% GGBS increased in length by the end of the testing programme.

Figure 5 shows that the CEM III/A cement had a slightly higher initial contraction than the others for the samples exposed to the sulphuric acid solution. However, the steel pins used to take the reading were damaged by the severity of the acid compromising the results from 3 months onwards. Each of the other mixes showed a consistent trend in terms of contraction at each monthly interval.

Figure 6 shows the change in length of all mixes reduced over time when exposed to the sodium sulphate solution, with the greatest change in length coming from the sulphate resisting cement mix.

3.2 *Mass loss – sulphuric acid exposure*

Figure 7 show the change in mass of the 150mm cubes exposed to sulphuric acid. Samples stored in water showed no change in mass throughout the testing while all samples lost mass for the first two months with each mix then alternating between mass loss and gain for the remaining four months. The

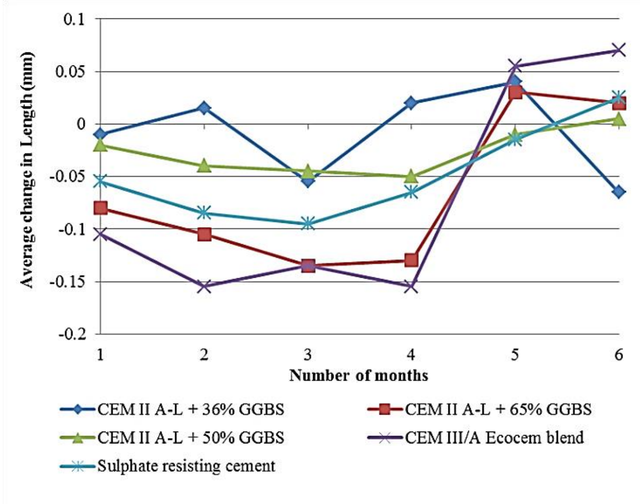

Figure 4. Average change in length – 280x75x75mm prisms exposed to water

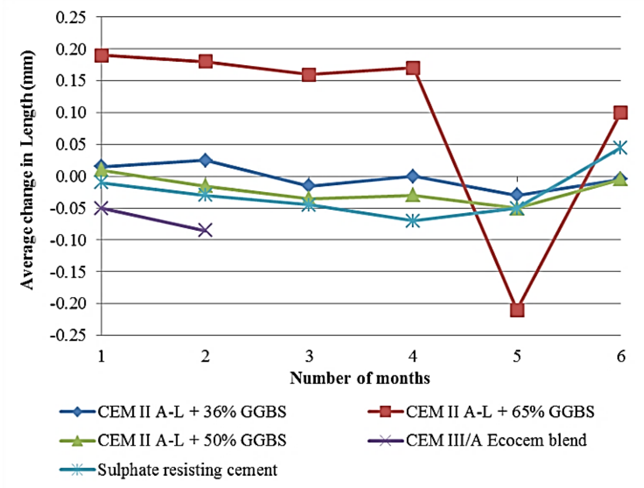

Figure 5. Average change in length – 280x75x75mm prisms exposed to sulphuric acid

CEM III/A showed the least variation in change of mass compared to the other mixes while the CEM II A-L + 65% GGBS showing the greatest variation.

3.3 *Strength Test – Water and sulphuric acid exposure*

Figures 8 show the average compressive strength of the cubes at 28 days and at 196 days for both exposed and control cubes. From this figure we can see that the CEM III/A mix had the highest strengths at each point in time. It can also be seen that the 196 day cubes immersed in the sulphuric acid solution were weaker than control samples at 196 days.

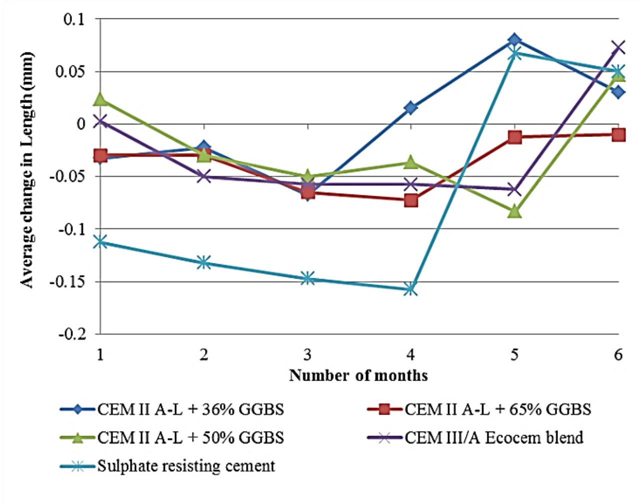

Figure 6. Average change in length - 280x75x75mm prisms exposed to sulphates

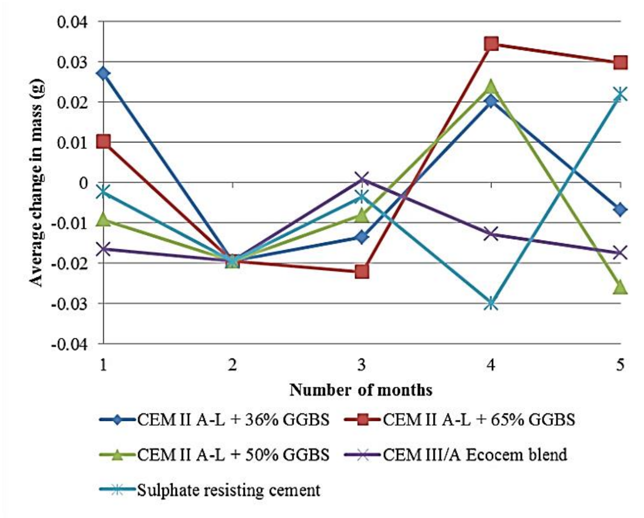

Figure 7. Change in mass - $150mm^3$ cubes exposed to sulphuric acid

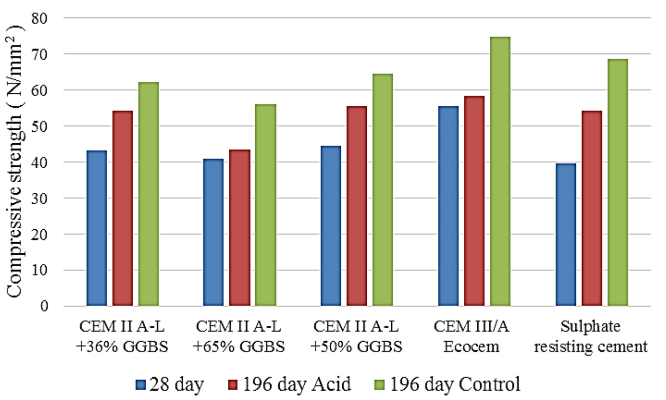

Figure 8: Compression test results

4 DISCUSSION

4.1 *Experimental results*

4.1.1 Expansion and contraction

All mixes showed a varying degree of expansion and contraction when exposed to sulphuric acid and sodium sulphate. The results show that samples kept in both solutions show a trend to contraction for 1-3 months with results towards the end of the testing programme showing expansion. The CEM III/A mix performed comparable to the other mixes in the sodium sulphate solution indicating that it is not negatively affected in these conditions.

4.1.2 Degradation of test specimens

Samples were also visually monitored throughout the testing programme in terms of surface degradation after brushing. Figure 9 shows a cube from mix 1, CEM II A-L +36% GGBS which demonstrated the worst surface degradation that had occurred.

All samples showed signs of gypsum formation on the surface of the concrete which may have contributed to the surface degradation. Care was also taken to ensure that the amount of brushing carried out on each sample was consistent but some samples appeared to withstand this abrasion more than others. Degradation was observed to some degree in all samples after the initial brushing with the CEM III/A performing particularly well.

Figure 9: Surface degradation of cube from mix 1

4.1.3 Mass loss

Mass loss was recorded 28 days after initial exposure of the cubes to the sulphuric acid solution. All cubes lost mass initially after the first 28 day cycle with all mixes then alternating between gaining and losing mass over remaining time of testing. The variation in mass changed quite significantly over the testing period with months 4 and 5 showing a high range in mass change for all mixes except CEM III/A. The CEM III/A showed the least variation in mass change compared to the other mixes for the duration of the testing. Previous studies utilising a similar mass loss method have shown varying results including a gradual decrease in mass over exposure time, [9] while others have shown samples increasing in mass initially and then decreasing [10, 11]. The relatively consistent results from the CEM III/A mix indicate that it may better resist the acidic conditions it was exposed compared to the other CEM II mixes.

4.1.4 Compressive strength

The results of the compressive tests show that the control samples kept in water were stronger than those samples kept in solutions. The CEM III/A mix had the highest 28 and 198 day strengths. Previous studies have shown that concrete compressive strength decreases after prolonged exposure to acids, [6, 9, 10]. While each of these studies used different mix designs the trend shows compressive decreasing. However, this study found an increase in compressive strength for all samples immersed in acid compared to the 28 day test. However, over time, all cubes exposed to acid were weaker than those kept in water including the CEM III/A cubes which shows that the sulphuric acid did negatively affect the final compressive strength of the cubes.

4.2 *Additional comments*

According to the results of this study the CEM III/A (Ecocem blend) is able to withstand the effects of harsh acid environments simulated in these laboratory experiments. The average contraction and expansion of this mix was less than S.R.C. for samples exposed to the sodium sulphate solution. The mass loss for the samples exposed to sulphuric acid was also the lowest of each of all mixes and in terms of compressive strength, CEM III/A cubes performed better than all other mixes after exposure to sulphuric acid.

5 CONCLUSION

Overall this study showed that CEM III/A performed comparatively well or better compared to other the mixes in terms of expansion/contraction, mass loss and compressive strength compared to the CEM II A-L mixes with varying percentages of GGBS and S.R.C. This agrees with the recommendation in BS 8500, the UK annex to EN 206 and the British Research Establishment (BRE) Special Digest 1, which recommends CEM III/A cement with a GGBS range of 36-65% for use in harsh acid environments as the results here show that CEM III/A would be suitable for use in these harsh acidic conditions.

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